ethylene dibromide in dry and moist soils at dosages approaching field applications of ethylene dibromide (4 to 6 gallons per acre). At present, this method shows particular usefulness in dry systems where the complicating factor of moisture is minimized.

### Literature Cited


(1) Hanson, W. J., *Advances in Chem. Ser.*, No. **1**, 202 (1950).
(2) Kolthoff, I. M., Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," 1st ed., p. 542, Macmillan, New York, 1936.
(3) Lubatti, O. F., Harrison, A., *J. Soc. Chem. Ind. (London)* **63,** 140 (1944).
(4) Wade, P., *J. Sci. Food Agr.* **5,** 194 (1954).



*Received for review July 10, 1959. Accepted October 12, 1959.*


**INSECTICIDE RESIDUES**

# Persistence of Dimethoate and Metabolites Following Foliar Application to Plants


**W. C. DAUTERMAN, G. B. VIADO[1], J. E. CASIDA, and R. D. O'BRIEN[2]**

**Department of Entomology, University of Wisconsin, Madison, Wis.**



Dimethoate [O,O-dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate] is known to be effective as a systemic insecticide following foliar application. Analyses were made of surface and absorbed residues following foliar treatment of corn, cotton, pea, and potato plants with radioactive dimethoate. The insecticide was rapidly absorbed and decomposed both on the surface and inside the foliage by phosphorothionate oxidation and hydrolysis. Only trace amounts of dimethoate and its oxygen analog were present 32 days after treatment. Of the five identified hydrolysis products, the predominant one from near mature peas was phosphoric acid and from the other plants used as seedlings was O,O-dimethyl S-carboxymethyl phosphorothiolate on the surface and O-methyl O-hydrogen S-(N-methylcarbamoylmethyl) phosphorodithioate within the leaf tissue. Limited studies were also made on the persistence of the N-ethyl analog of dimethoate.


DIMETHOATE [*O,O*-dimethyl *S*-(*N*-methylcarbamoylmethyl) phosphorodithioate] is active as a systemic insecticide for grub control in cattle (*6*). This same chemical (designated as Rogor in England and Europe) has been used for insect control on plants for several years (*12, 13*). It displays good systemic activity following foliar application (*2*) and as a side dressing in the soil when formulated on granules (*11*). The oxygen analog of dimethoate [*O,O*-dimethyl *S*-(*N*-methylcarbamoylmethyl) phosphorothiolate] has been demonstrated in bean and cherry plants after root and foliar dimethoate treatment, respectively (*12, 13*). Studies on the mammalian metabolism of dis methoate were reported in a previou paper (*5*).

The present investigation concerns the persistence and metabolites associated with the use of dimethoate as a systemic insecticide for treating plant foliage.

[1] Present address, Department of Entomology, University of the Philippines, Laguna, Philippines.
[2] Present address, Pesticide Research Institute, Canada Department of Agriculture, London, Ontario, Canada.

### Methods

**Dimethoate Derivatives Utilized.** In addition to dimethyl phosphoric, phosphorothioic, and phosphorodithioic acids, the following compounds related to dimethoate were studied: *O,O*-dimethyl *S*-(*N*-methylcarbamoylmethyl) phosphorothiolate, $(CH_3O)_2P(O)SCH_2C(O)NHCH_3$, the oxygen analog of dimethoate; *O,S*-dimethyl *S*-(*N*-methylcarbamoylmethyl) phosphorothiolate, $(CH_3O)(CH_3S)P(O)SCH_2C(O)NHCH_3$, the *S*-methyl isomer of dimethoate; *O,O*-dimethyl *S*-carboxymethyl phosphorodithioate, $(CH_3O)_2P(S)SCH_2C(O)OH$, the thio-carboxy derivative of dimethoate; *O,O*-dimethyl *S*-carboxymethyl phosphorothiolate, $(CH_3O)_2P(O)SCH_2C(O)OH$, the oxy-carboxy derivative of dimethoate; *O*-methyl *O*-hydrogen *S*-(*N*-methylcarbamoylmethyl) phosphorodithioate, $(CH_3O)(HO)P(S)SCH_2C(O)NHCH_3$, the des-methyl derivative of dimethoate; and *O,O*-dimethyl *S*-(*N*-ethylcarbamoylmethyl) phosphorodithioate, $(CH_3O)_2P(S)SCH_2C(O)NHC_2H_5$, the *N*-ethyl analog of dimethoate which is designated as CL 18,706.

**Synthesis.** Radioactive dimethoate was prepared, purified, and characterized as previously described (*5*) using isotopic exchange to obtain the phosphorus-32 pentasulfide intermediate (*4*). The radioactive product was identical in infrared spectrum with highly purified dimethoate and had a specific activity of about 25 mc. per gram. Radioactive CL 18,706 was prepared in 60% yield by the same procedure as for dimethoate, except that *N*-ethyl α-chloroacetamide replaced *N*-methyl α-chloroacetamide. The radioactive product was identical in chromatographic properties and infrared spectrum with a highly purified sample of known CL 18,706.

**Volatilization.** The volatilization rates for radioactive dimethoate from cotton leaves and the surfaces of metal, wood, glass, plastic, rubber, Masonite, and Pressboard were determined. Approximately 5 γ of radioactive dimethoate in 0.1 ml. of acetone were applied to the upper leaf surface of each cotton plant in a spot 0.5 inch in diameter, or to comparable areas of the other surfaces. The treatments were replicated six times and the materials were held in a greenhouse at about 28° C. Radioassays (*7*) were made periodically after treatment.

The volatilization rate for radioactive

CL 18,706 from cotton leaves was also determined using the same technique.

**Persistence and Absorption.** Potted seedlings of corn (variety 1512), cotton (Lankart 55), and potato (Irish cobbler) with above-ground heights of 6, 4, and 6 inches, respectively, were treated by dipping the plants into a solubilized dimethoate solution composed of 30 mg. of phosphorus-32 dimethoate, 3.26 mg. of Alrodyne 315, 3.26 mg. of Aerosol OT, and 8.70 mg. of methyl Cellosolve per 50 ml. of water. This formulation was equivalent to about 0.5 pound of dimethoate per 100 gallons of water. Four plants of each species were periodically removed for analysis. The leaf surfaces were washed with 20 ml. of water followed by two 20-ml. portions of acetone. The acetone wash fractions were combined and stripped of solvent, and the residue was dissolved in the water fraction from the surface wash. Leaves from each individual washed sample were then weighed and 2 to 4 grams were homogenized with 7 ml. of water in a Potter-Elvehjem glass homogenizer. Total radioactivity was determined for each fraction. Four milliliters of the surface wash and the leaf homogenate, respectively, were partitioned against an equal volume of chloroform to determine the per cent chloroform-solubles. The same procedure was used for seedling cotton plants treated with radioactive CL 18,706 and for near mature pea plants (Perfection 15 variety) treated with phosphorus-32 dimethoate.

**Chemical Changes in Dimethoate on the Plant Surface.** Corn, potato, and cotton plants were fractionated as described above at 2 and 12 days after treatment, while peas were fractionated only at 12 days after treatment. Partition chromatography with silica gel columns (*5*, *14*) was utilized to separate the dimethoate derivatives which partitioned into chloroform from neutral aqueous solutions, and ion exchange chromatography (*8*) was used to separate the water-soluble metabolites from the same extractions. Resolution with the ion exchange chromatograms was greatly improved over a previous study (*5*) by substituting cylinders (*3*) for separatory funnels in the gradient elution apparatus (*8*). To obtain sufficient radioactivity, the surface washes from three plants were combined before being chromatographed.

**Stability of Dimethoate on Glass Surfaces.** One hundred micrograms of radioactive dimethoate in 2 ml. of acetone were added to a Petri dish and the solvent was evaporated. The same amount of the compound was also added to a Petri dish containing a surface extract of potato leaves obtained by scrubbing the leaves with acetone, chloroform, and benzene and then allowing this combined extract to evaporate in the dish. After 7 days of exposure in the greenhouse at approximately 28° C. the per cent hydrolysis was determined by a chloroform-water partition and the chloroform-solubles were fractionated by partition chromatography.

**Metabolism of Dimethoate Absorbed by Leaves.** Using the above described techniques, the surface residues at 2 and 12 days after treatment were removed by washing with water and acetone. These leaves which were free of surface residue were then homogenized with 7 ml. of water in a Potter-Elvehjem glass homogenizer and the homogenate was partitioned with an equal volume of chloroform. The chloroform-soluble metabolites were fractionated on a silica gel column and the water-soluble metabolites on an ion exchange column.

**Dimethoate Residues in Peas.** Flowering pea plants (Perfection 15 variety) were sprayed with radioactive solubilized dimethoate to yield an initial residue of 25 p.p.m. based on the wet weight of the whole plant. Immediately after treatment, four whole plants were fractionated, and 17 days after treatment an additional four plants were separated into pods and nonfruiting tissues which were analyzed separately. Extraction consisted of homogenizing the tissue in a Waring Blendor with 100 ml. each of water and chloroform followed by centrifugation to separate the water, chloroform, and insoluble residue fractions. This residue was re-extracted with 100 ml. of acetone and after the solvent was stripped the acetone-soluble materials were added to the chloroform. Total radioactivity was determined for each fraction, including the residue which was first predigested in nitric acid to allow more efficient counting. Using the fractionation system just described, untreated pea samples to which 1 p.p.m. of dimethoate was added gave recovery rates of 85 and 93% for the pods and plants, respectively.

**Other Methods.** Other techniques not discussed in detail were the same as in a previous study on dimethoate (*5*).

## Results and Discussion

**Volatilization.** Dimethoate was lost from the surface of treated cotton leaves at the rate indicated in Figure 1. Approximately 58% of the total dimethoate equivalents were lost during the first 10 days with no substantial loss thereafter. The rate of CL 18,706 loss from cotton leaves was similar to that of dimethoate (Figure 1), the major loss occurring during the first 10 days and amounting to 63% of that initially applied. Loss of total dimethoate equivalents from the surface of metal, plastic, rubber, and glass followed first-order kinetics. The number of days until one-half volatilization had occurred was 35, 39, 71, and 130, respectively, for the surfaces. With wood, Masonite, and Pressboard the rate of dimethoate volatilization was too low to be accurately measured.

The major loss recorded by this technique was probably by volatilization. However, with cotton leaves some loss also occurred from penetration into the leaf resulting both in self-absorption of the beta-radiation by the leaf tissue and partial translocation of the material away from the area assayed (*13*). Codistillation may have also been involved in the residue loss from plants.

**Persistence and Absorption.** Dimethoate residues in and on plant leaves were dissipated at the rate indicated in Table I, this loss resulting both from volatilization and increase in plant weight from growth. The total parts per million of dimethoate equivalents diminished most rapidly with corn.

As shown in Figure 2, solubilized dimethoate rapidly penetrated into the foliage of corn, cotton, and potato. From the data in Table I and Figure 2 it is possible to calculate the actual parts per million in each fraction of the leaf. For example, at 32 days after treatment of potato foliage there were 4.8 p.p.m. total dimethoate equivalents on the surface and 23.2 p.p.m. inside the potato leaf. As for the chloroform-soluble dimethoate derivatives, 0.1 p.p.m. was found on the surface in contrast to 0.46 p.p.m. inside the leaf at this time.

Similarly, on cotton and potato foliage dimethoate penetrated rapidly and the breakdown was much slower on the surface than inside the leaf (Figure 2). It seemed to be metabolized more slowly in cotton than potato, as at 8 days there were 18% as chloroform-solubles inside the cotton leaf but only 7% in potato. CL 18,706 also penetrated rapidly into

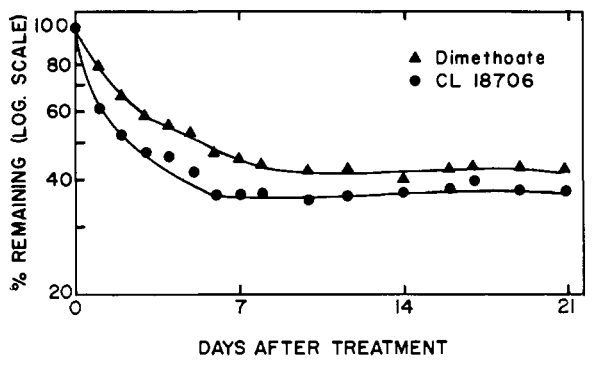


Figure 1. Per cent of total applied dimethoate and CL 18,706 equivalents persisting on and in cotton leaves

cotton foliage with slower degradation on the surface than inside the leaf (Figure 2). Comparing the two compounds at 32 days after treatment of cotton, the amount of chloroform-solubles was similar, but the per cent of the total applied equivalents on the surface was about 20% for dimethoate and 12% for CL 18,706, indicating a somewhat more rapid penetration of CL 18,706.

Of the plant species studied, the rate of penetration of dimethoate into the leaf was the slowest with corn (Figure 2). The rate of metabolism inside the corn leaf was much faster than with potato or cotton as shown by the rate of decrease of the chloroform-soluble materials, but the surface alteration was the slowest.

**Chemical Changes in Dimethoate on Plant Surface.** For evaluation of residue data it is essential to know the composition as well as the total level of residues. Column chromatography of the chloroform-soluble compounds on the surface 2 and 12 days after treatment showed that in addition to dimethoate a compound eluting with 100% chloroform was present. The first radioactive peak was characterized as dimethoate based on chromatography with known carrier compound and similar rates of hydrolysis of the radioactive component and the carrier in 0.1*M* aqueous sodium carbonate as ascertained by chloroform-water partitioning after various incubation times. The second peak was found to co-chromatograph with the known oxygen analog and not with the *S*-methyl isomer of dimethoate. Paper chromatography with 85 to 15 acetonitrile-water also showed co-chromatography of the second peak from the column with the known oxygen analog, both having an $R_f$ value of 0.74. Therefore oxidation and not isomerization was the principal nonhydrolytic alteration in dimethoate on the surface. The per cent of oxygen analog (Table II) was similar for all the plant species with respect to the surface residues.

The amount of dimethoate, oxygen analog, and water-soluble derivatives on the surface 2 and 12 days after treatment of potato is shown in Table III. With the longer time interval there was a decrease in the total amount of oxygen analog on the surface but an increase in the proportionate amount with respect to dimethoate (Table II). The decrease in total dimethoate equivalents between 2 and 12 days is partially attributable to a loss from the surface by absorption, volatilization, and possibly co-distillation.

The water-soluble derivatives on the surface of corn, cotton, and potato were fractionated by ion exchange chromatography into four materials (Table IV). Dimethyl phosphoric acid, *O,O*-dimethyl phosphorothioic acid, and the des-methyl derivative of dimethoate were identified by co-chromatography with known carrier compounds. The fourth material was probably the oxy-carboxy derivative of dimethoate based on the following evidence: not extracted by chloroform at pH 7 but readily extracted at pH 1.3 suggesting that the material is a weak acid; co-chromatography on an ion exchange column with a minor product (7.6%) from the hydrolysis of the oxygen analog of dimethoate in 1*N* hydrochloric acid for 12 hours at 28° C.; and co-chromatography on an ion exchange column with a product formed in 26% yield by bubbling nitrogen tetroxide ($N_2O_4$) through a carbon tetrachloride

**Table I. Persistence of Dimethoate and CL 18,706 or Their Metabolites on and in Plant Foliage**

| Days after Treatment | Dimethoate[a] Corn | Peas | Potato | Cotton | CL 18,706[a] Cotton |
|---|---|---|---|---|---|
| 0 | 246 (195–298)[b] | 129 (112–150) | 791 (590–1040) | 65 (55–72) | 66 (58–75) |
| 4 | 24 (9–46) | ... | 428 (300–500) | 28 (24–32) | 50 (40–65) |
| 12 | 7.0 (5–10) | 34 (32–40) | 98 (75–180) | 20 (16–22) | 25 (19–31) |
| 32 | ... | ... | 28 (16–39) | 7.0 (5–10) | 10 (9–12) |

[a] Figures represent total parts per million of dimethoate or of CL 18,706 equivalents.
[b] Numbers in parenthesis give the range (four replicates).

**Table II. Per Cent of Chloroform-Soluble Dimethoate Equivalents as Oxygen Analog of Dimethoate**

(Remainder as dimethoate)

| | Corn | Peas | Potato | Cotton |
|---|---|---|---|---|
| Surface | | | | |
| 2 days | 0.9 | ... | 0.9 | 0.8 |
| 12 days | 5.4 | 4.8 | 6.3 | 6.8 |
| Internal | | | | |
| 2 days | 1.4 | ... | 3.9 | 3.4 |
| 12 days | 11.8 | 10.5 | 25.0 | 8.8 |

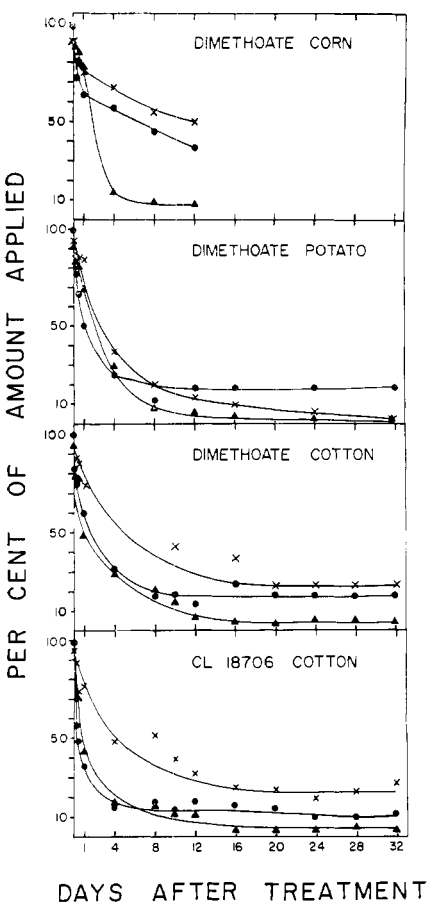


Figure 2. Persistence of dimethoate on or in leaves of cotton, potato, and corn and CL 18,706 on or in cotton foliage

● % total residue on surface
× % surface residue as chloroform-soluble dimethoate equivalents
▲ % absorbed residue as chloroform-soluble dimethoate equivalents

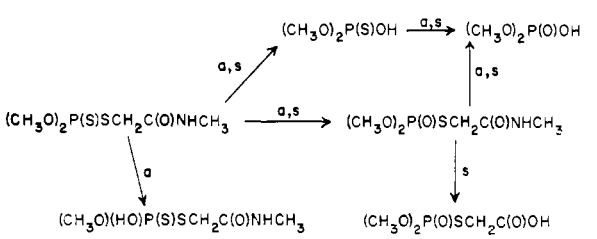


Figure 3. Proposed metabolic pathway for 0,0-dimethyl S-(N-methylcarbamoyl-methyl) phosphorodithioate applied to surface of corn, cotton, and potato

*a.* Reactions of absorbed residues, presumably enzymatic
*s.* Reactions of surface residues, presumably nonenzymatic
This decomposition pathway does not incorporate the large amount of phosphoric acid formed in peas

**Table III. Nature of Residues from Dimethoate Applied to Potatoes**

| Days after Treatment | Surface | | | Internal | | |
|---|---|---|---|---|---|---|
| | Dimethoate | Oxygen analog | $H_2O$ sol. | Dimethoate | Oxygen analog | $H_2O$ sol. |
| 2 | 77.5 | 0.7 | 11.1 | 27.8 | 1.7 | 39.7 |
| 12 | 1.3 | 0.1 | 6.2 | 2.0 | 0.6 | 50.2 |

Results expressed as micrograms of total dimethoate equivalents per plant rather than as p.p.m. to minimize changes resulting from increase in plant weight due to growth.

**Table IV. Composition of Water-Soluble Metabolites on Plant Surface 2 and 12 Days after Treatment**

(Expressed as per cent)

| | $H_3PO_4$ | $(MeO)_2P(O)OH$ | Oxy-Carboxy Derivative | $(MeO)_2P(S)OH$ | Des-methyl Derivative |
|---|---|---|---|---|---|
| 2 days | | | | | |
| Corn | 0.0 | 3.2 | 77.4 | 9.0 | 10.5 |
| Potato | 0.0 | 0.7 | 93.8 | 2.7 | 2.6 |
| Cotton | 0.0 | 2.4 | 94.1 | 2.5 | 1.1 |
| 12 days | | | | | |
| Corn | 0.0 | 6.3 | 87.5 | 2.7 | 3.5 |
| Pea | 51.7 | 7.6 | 8.8 | 11.3 | 20.7 |
| Potato | 0.0 | 4.4 | 81.0 | 6.0 | 8.6 |
| Cotton | 0.0 | 6.2 | 70.9 | 4.6 | 18.3 |

**Table V. Composition of Water-Soluble Metabolites Inside Leaves 12 Days after Treatment**

(Expressed as per cent)

| | $H_3PO_4$ | $(MeO)_2P(O)OH$ | Oxy-Carboxy Derivative | $(MeO)_2P(S)OH$ | Des-methyl Derivative |
|---|---|---|---|---|---|
| Corn | 0.0 | 13.8 | 4.1 | 17.8 | 64.3 |
| Pea | 47.8 | 12.0 | 5.7 | 16.8 | 17.7 |
| Potato | 0.0 | 25.9 | 10.4 | 18.4 | 45.3 |
| Cotton | 0.0 | 12.8 | 5.4 | 12.6 | 69.2 |

Results for homogenates of leaves washed to remove surface metabolites.

solution of the thio-carboxy derivative of dimethoate at 0° to 10° C., a procedure which oxidized the thiono group based on infrared evidence. From large amounts of plant foliage 300 $\gamma$ of this fourth radioactive material were recovered, but attempts to separate the compound from 2 mg. of nonradioactive impurities in order to obtain an interpretable infrared spectrum were unsuccessful. The major water-soluble derivative of dimethoate on the surface 2 and 12 days after treatment was the oxy-carboxy compound (Table IV). With these three plant species only dimethyl phosphoric acid definitely increased in proportion during the 2- to 12-day period.

On the leaf surface of mature pea plants five water-soluble derivatives were found, the major one being phosphoric acid (Table IV).

**Stability of Dimethoate on Glass Surfaces.** The extensive hydrolysis and partial oxidation of dimethoate on the leaf surfaces might result from a general surface phenomenon or might be unique for the plant surface due to catalytic or reactive materials from the leaf or by excretion onto the surface of materials which had been produced by metabolism inside the leaf. To differentiate these mechanisms, dimethoate was added to glass surfaces, and to glass surfaces treated with a surface wash from potato leaves (see Methods). Some degradation occurred in both cases in 7 days. The plain surfaces had 11% of the total as hydrolysis products and 1.5% of the chloroform-solubles as oxygen analog. The corresponding figures for the treated surface were 19 and 1.1%. The reactions on the plant leaf are therefore largely attributable to nonspecific effects, although the possibility remains that hydrolysis is catalyzed by a component of the leaf surface. The variety of dimethoate metabolites which appear on the leaf surface probably results, at least in part, from the excretion onto the surface of metabolites formed within the leaf.

**Metabolism of Dimethoate Absorbed by Leaves.** Chromatography of the chloroform-soluble compounds inside the leaf at 2 and 12 days after treatment gave two radioactive peaks which were identified as dimethoate and its oxygen analog by chromatography with known carrier compounds. Based on the per cent of oxygen analog formed inside the leaf (Table II), the potato seems to have the best ability to oxidize dimethoate.

From these findings it was possible to calculate the amount of dimethoate, oxygen analog, and water-soluble metabolites inside the potato leaf 2 and 12 days after treatment (Table III). There was a decrease with time in the total amount of oxygen analog inside the leaf, but a proportionate increase with respect to dimethoate (Table II). The decrease in total micrograms of dimethoate equivalents between 2 and 12 days presumably reflects some form of redistribution, volatilization and/or excretion. The data on the chloroform-soluble materials show that it is essential for a residue analysis method to determine both dimethoate and the oxygen analog, although it may not be necessary to distinguish between them.

Analysis of the water-soluble metabolites in the leaves of corn, cotton, and potato showed the same four materials which were found for the surface wash but in different proportions (Table V). Whereas on the leaf surface the oxy-carboxy compound predominated, inside the leaf the des-methyl metabolite was found in the greatest amount. In potato there was a larger percentage of dimethyl phosphoric acid and a lesser percentage of des-methyl derivative than in cotton and corn. The major water-soluble metabolite found in mature pea leaves was phosphoric acid and the other derivatives were present in about the same proportions on the surface as within the leaf. The contribution of *O*-methyl *O* - hydrogen *S* - (*N* - methylcarbamoylmethyl) phosphorothiolate, the des-methyl derivative of the dimethoate oxygen analog, to these results is not known, as the pure compound was not available to determine its position of elution.

**Dimethoate Residues in Peas.** The chloroform-soluble dimethoate equivalents from pea plants treated in the flowering stage dropped from 25 p.p.m. initial over-all residue to 0.3 p.p.m. for the pea pods and 0.5 p.p.m. for the remaining plant tissue by harvest at 17 days. Water-soluble dimethoate equivalents comprised 1.8 p.p.m. of the pods and 6.7 p.p.m. of the remaining plant tissue, while the unextractable residue fraction contained 1.1 p.p.m. dimethoate equivalents for the pods and 1.4 p.p.m. for the other tissues.

## Conclusions

The formation of the oxygen analog of dimethoate on the surface of leaves is probably a nonenzymatic oxidation as it can be duplicated when dimethoate is exposed to the atmosphere in a thin layer on nonbiological surfaces. However, the high levels of oxygen analog internally suggest that enzymatic oxidation also occurs. This is also suggested by the observation that oxygen analog is formed within the plant following systemic treatment via the roots (*12, 13*).

The marked quantitative difference found in the levels of the different water-soluble derivatives on the surface and in the leaves of young corn, cotton, and potato plants suggests quite different mechanisms of degradation. As no *O,O*-dimethyl phosphorodithioic acid was found in any case, both enzymatic and nonenzymatic attack on the P—S—C bond probably occurs at the P—S rather than at the S—C linkage. Alternate explanations for the absence of this dithioic acid would be that it was rapidly

oxidized after formation or that the hydrolysis of the P—S—C bond in dimethoate always follows a preliminary phosphorothionate oxidation.

Hydrolysis at the alkoxy group occurred mainly inside leaves of corn, cotton, and potato, indicating an enzymatic action at this site. Degradation at the alkoxy group has been reported for mammals (*5, 7, 9, 10*), but this is the first similar observation in plants.

Hydrolysis in and on the surface of mature pea plants was greatly different from the other plants in that phosphoric acid was the major derivative formed in peas but was absent in corn, cotton, and potatoes. The explanation of this striking difference with peas is not known.

When dimethoate was administered to mammals, the major metabolite excreted was the thio-carboxy derivative (*5*). As none of this derivative was found in or on plants, the formation of the oxy-carboxy derivative probably proceeded by oxidation of dimethoate to its oxygen analog first and then by hydrolysis of the carbamoyl group. As the oxy-carboxy derivative was found in largest amount on the surface, the carbamoyl bond cleavage was probably nonenzymatic and it is unnecessary to postulate an enzyme hydrolyzing the C—N bond of this compound in plants.

In a previous study on dimethoate metabolism in mammals (*5*), no oxygen analog was isolated although there was indirect evidence for its formation. The plant studies reported here were made with a phosphorus-32 dimethoate sample of five times greater specific activity, which may partially account for the ability to detect the oxygen analog in plants but not mammals. An unidentified dimethoate metabolite reported in the mammalian study and designated as "unknown A" (*5*) has the same properties as the oxy-carboxy derivative found in plants.

The pathway of dimethoate degradation in plants is summarized in Figure 3.


### Acknowledgment

The authors are indebted to Lydia McBride, Kay Matthews, Mary Snell, and Judy Rhyner for skilled technical assistance. The advice and assistance of R. W. Young and G. L. Sutherland of the American Cyanamid Co., Stamford, Conn., are also gratefully acknowledged. The authors are further indebted to R. W. Young for supplying certain of the organophosphates used in this study.


### Literature Cited


(1) Ahmed, M. K., Casida, J. E., *J. Econ. Entomol.* **52,** 111 (1959).
(2) American Cyanamid Co., Stamford, Conn., "Experimental Insecticides 12,880 and 18,706," Bulletin, 12 pp., January 1958.
(3) Bock, R. M., Ling, N. S., *Anal. Chem.* **26,** 1543 (1954).
(4) Casida, J. E., *Acta Chem. Scand.* **12,** 1691 (1958).
(5) Dauterman, W. C., Casida, J. E., Knaak, J. B., Kowalczyk, Tadeusz, J. AGR. FOOD CHEM. **7,** 188 (1959).
(6) Hewitt, R., Brebbia, A., Waletzky, E., *J. Econ. Entomol.* **51,** 126 (1958).
(7) Krueger, H. R., Casida, J. E., Niedermeier, R. P., J. AGR. FOOD CHEM. **7,** 182 (1959).
(8) Plapp, F. W., Casida, J. E., *Anal. Chem.* **30,** 1622 (1958).
(9) Plapp, F. W., Casida, J. E., J. AGR. FOOD CHEM. **6,** 662 (1958).
(10) Plapp, F. W., Casida, J. E., *J. Econ. Entomol.* **51,** 800 (1958).
(11) Reynolds, H. T., Metcalf, R. L., Entomol. Soc. Am., 6th annual meeting, Salt Lake City, Utah, December 1958.
(12) Santi, R., de Pietri-Tonelli, P., *Nature* **183,** 398 (1959).
(13) Santi, R., de Pietri-Tonelli, P., "Richerche sul meccanismo d'azione della *N*-monometilammide dell' acido *O,O*-dimetilditiofosforilacetico," Montecatini, Milano, Italy, Bulletin, 1959.
(14) Tsuyuki, H., Stahmann, M. A., Casida, J. E., J. AGR. FOOD CHEM. **3,** 922 (1955).



*Received for review August 10, 1959. Accepted October 7, 1959. Approved for publication by the Director of the Wisconsin Agricultural Experiment Station. Study supported in part by research grants from the American Cyanamid Co., U. S. Atomic Energy Commission [Contract No. AT(11-1), project No. 14], and Regional Research Project N.C. 33.*


**PESTICIDE RESIDUES**

# Rapid Combustion and Determination of Residues of Chlorinated Pesticides Using a Modified Schöniger Method


**DONALD J. LISK**

**Pesticide Residue Laboratory, Department of Entomology, New York State College of Agriculture, Cornell University, Ithaca, N. Y.**


CHLORINE has been removed from chlorinated pesticides prior to their determination as residues, by combustion and sodium reduction. Schöniger (*2, 3*) used an oxygen-filled flask to burn samples in a rapid combustion method for the microdetermination of halogens and sulfur in organic compounds. In the work reported, an oxygen-filled flask with a balloon attached for pressure control is used for combustion of residues of chlorinated pesticides.

A benzene extract of alfalfa containing the pesticide is evaporated in a cone of cellulose acetate. The cone and contents are burned in the flask and the hydrogen chloride gas is absorbed in dilute sodium hydroxide. A specially designed platinum holder permits complete combustion of the residue with no carbon formation. Chloride is determined spectrophotometrically by an adaptation of the method of Bergmann and Sanik (*1*) involving displacement of thiocyanate by chloride in the presence of ferric ion.

### Description of Combustion Flask

The combustion flask and platinum holder are illustrated in Figure 1 (*A* and *B*).

A 1-liter borosilicate glass Erlenmeyer flask with a 34/28 standard-taper, female ground joint sealed on the neck is used. A side arm (1.5 cm in outside diameter, 7 cm. long) is sealed to the flask at the base of the shoulder as shown. A rubber balloon about 7 cm. long is secured to the side arm with string. A small rubber band is placed on the arm as shown.

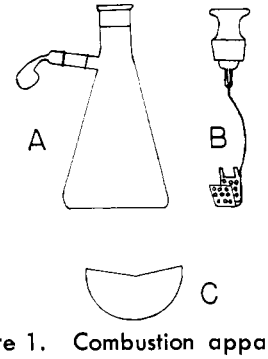


Figure 1. Combustion apparatus
A. Flask
B. Platinum holder
C. Plastic cone template

The platinum holder is constructed by sealing a 13-cm. length of No. 16 B and S gage platinum wire onto a 34/28